REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-98

0569

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
		FINAL 15 Jun 95 To 14 Jun 98

4. TITLE AND SUBTITLE

NANOMETRIC STUDIES OF THE STRUCTURE AND TRIBOLOGY OF CARBON NITRIDE MATERIALS

5. FUNDING NUMBERS

F49620-95-1-0423

3484/YS

61103D

6. AUTHOR(S)

DR CHARLES M. LIEBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Dept of Chemistry & Chemical Biology
Harvard University
12 Oxford Street
Cambridge MA 02138

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NL
110 Duncan Ave Room B115
Bolling AFB DC 20332-8050

Maj Hugh C. De Long

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Significant effort has been placed on several areas. First, we have carried out systematic studies of the growth of carbon nitride materials as a function of carbon reactant enegetics, nitrogen flux and growth temperature and have quantitatively analyzed the structrue and local bonding in these materials. The emphasis of these studies has been to determine unambiguously conditions that can produce sp3-bonding since this is required for a superhard coating. Significantly, we have show recently that there is a nitrogen-driven sp3 to sp2 structural transformation in the carbon nitride materials as nitrogen content is increased about 15 atomic percent. With these limits worked out we ahve also prepared films with optimal C-N ratios for hardness, and investigated their nanotribological properties by force microscopy. In addition, we have carried out theoreticalcluster calculations to understand the origin of this sp3 to sp2 transition. Significantly, these calculations demonstrate that the transition is an intrinsic property of carbon nitride system since (i) the sp2 bonded structure becomes thermodynamically favored for 15% nitrogen and (ii) the barrier between sp3 and sp2 structures also reduces significantly for 15% nitrogen.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
(U)	(U)	(U)	(UL)

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

FINAL TECHNICAL REPORT

15 JUNE 1995 TO 14 JUNE 1998

FOR

GRANT NUMBER: F49620-95-1-0423

AASERT95

"Nanometric Studies of the Structure and Tribology

of Carbon Nitride Materials"

Charles M. Lieber
Principal Investigator

Harvard University

Department of Chemistry and Chemical Biology
12 Oxford Street
Cambridge, MA 02138

Submitted:
31 July 1998

I. OBJECTIVES

The overall objective of this project has been to understand the growth and tribological properties of carbon nitride thin films. To achieve this objective we have pursued combined studies that involve systematic growth, structural measurements and nanotribology studies with our atomic force microscope. In addition, we have over the past year expanded the scope of these studies to include investigations of the synthesis and nanomechanical properties of nanowhisker materials. This new direction was pursued as a target of opportunity that exploited the expertise developed in synthesis and lateral/friction force measurements. Because these materials should represent unique components for high-performance composites critical to AFOSR technology, we believe this direction is worthwhile.

II. STATUS OF EFFORT

Significant effort has been placed on several areas. First, we have carried out systematic studies of the growth of carbon nitride materials as a function of carbon reactant enegetics, nitrogen flux and growth temperature and have quantitatively analyzed the structure and local bonding in these materials. The emphasis of these studies has been to determine unambiguously conditions that can produce sp^3-bonding since this is required for a superhard coating. Significantly, we have show recently that there is a nitrogen-driven sp^3 to sp^2 structural transformation in the carbon nitride materials as nitrogen content is increased about 15 atomic percent. With these limits worked out we have also prepared films with optimal C-N ratios for hardness, and investigated their nanotribological properties by force microscopy. In addition, we have carried out theoretical cluster calculations to understand the origin of this sp^3 to sp^2 transition. Significantly, these calculations demonstrate that the transition is an intrinsic property of carbon nitride system since (i) the sp^2 bonded structure becomes thermodynamically favored for 15% nitrogen and (ii) the barrier between sp^3 and sp^2 structures also reduces significantly for 15% nitrogen.

In addition, we have synthesized new nanoscale whisker materials, nanorods and nanowires, and developed a novel method to probe the mechanical properties of these materials. Significantly, we have used lateral force microscopy to measure the Young's modulus, strength and toughness of nanorods, wires and tubes for the first time. We have shown that the strength of SiC nanorods is 5-10 times greater than observed previously in micron diameter whiskers, and thus these materials should represent unique materials for next generation superstrong, supertough composites.

III. ACCOMPLISHMENTS/NEW FINDINGS

1. We have discovered and characterized a nitrogen driven sp^3 to sp^2 structural transformation in carbon nitrides materials. For nitrogen compositions greater than 15 atomic percent we have shown that the observable carbon nitride phase contains graphite-like bonding. Theoretical calculations have further shown that this structural transformation is intrinsic to the carbon nitride system and arises from an increased thermodynamic stability of the sp^2 structure and a reduction of the barrier between sp^3 and sp^2 structures. These studies are of major significance to the carbon nitride field since they define for the first time conditions where different types of materials (hard vs. soft) can be obtained on basic scientific grounds.

2. We have developed a lateral force microscopy technique that can characterize the elastic modulus, strength and toughness of nanorods, nanowires and nanotubes for the first time. We have used this technique to characterize the modulus and strength of SiC nanorods and have shown that these nanorods are the strongest known material. These results are of great significane to the emerging field of nanoscale materials, and have significant implications for the design of high-performance composites used in Air Force and civilian technologies.

IV. PERSONNEL SUPPORTED.

1. Paul Sheehan, graduate student

V. PUBLICATIONS SUPPORTED BY AASERT.

1. D.V. Vezenov, A. Noy, L.F. Rozsnyai and C.M. Lieber, "Force Titrations and Ionization State Sensitive Imaging of Functional Groups in Aqueous Solutions by Chemical Force Microscopy", *J. Am. Chem. Soc.* **119**, 2006-2015 (1997).

2. P. Yang, Z.J. Zhang, J. Hu and C.M. Lieber, "Pulsed Laser Deposition of Diamond-Like Carbon Thin Films: Ablation Dynamics and Growth", *Mat. Res. Soc. Symp. Proc.* **438**, 593-598 (1997).

3. A. Noy, D.V. Vezenov, and C.M. Lieber, "Chemical Force Microscopy", *Annu. Rev. Mater. Sci.* **27**, 381-421 (1997).

4. C.M. Lieber, D. Vezenov, A. Noy and C. Sanders, "Chemical Force Microscopy", *Microscopy and Microanalysis* **3**, 1253-1254 (1997).

5. E.W. Wong, P.E. Sheehan and C.M. Lieber, "Nanobeam Mechanics: Elasticity, Strength and Toughness of Nanorods and Nanotubes", *Science* **277**, 1971-1975 (1997).

6. J. Hu, P. Yang and C.M. Lieber, "Nitrogen-driven sp^3 to sp^2 transformation in carbon nitride materials", *Physical Review B* **57**, 3185-3188 (1998).

7. A. Noy, C.H. Sanders, D.V. Vezenov, S.S. Wong and C.M. Lieber, "Chemically-Sensitive Imaging in Tapping Mode by Chemical Force Microscopy: Relationship Between Phase Lag and Adhesion", *Langmuir* **14**, 1508-1511 (1998).

8. D.V. Vezenov, A. Noy and C.M. Lieber, "Chemical Force Microscopy: Probing and Imaging Interactions Between Functional Groups", in *Proceedings of the Scanning Probe Microscopy in Polymers Symposium* , 312-320 (American Chemical Society: Washington, DC, 1998).

9. J. Hu, P. Yang and C.M. Lieber, "Nitrogen driven structural transformation in carbon nitride materials", Proceedings of the Fourth International Conference on Laser Ablation, 569-573 (Elsevier Science: New York, NY, 1998).

10. S.S. Wong, E. Joselevich, A.T. Woolley, C.L. Cheung and C.M. Lieber, "Covalently functionalized nanotubes as nanometer probes for chemistry and biology", *Nature* **394**, 52-54 (1998).

11. C.M. Lieber, "One-Dimensional Nanostructures: Chemistry, Physics & Applications", *Solid State Communications* **107**, 607-616 (1998), in press.

12. S.S. Wong, A.T. Woolley, E. Joselevich, C.L. Cheung and C.M. Lieber, "Covalently-Functionalized Single-Walled Carbon Nanotube Probe Tips for Chemical Force Microscopy", *J. Am. Chem. Soc.* (1998), in press.

VI. INTERACTIONS/TRANSITIONS.

A. PRESENTATIONS AT MEETINGS, CONFERENCES AND SEMINARS.

1. "Force Microscopy Studies of Tribology at the Nanometer Scale: Probing the Molecular Origins of Friction", Air Force Office of Scientific Research/Office of Naval Rearch Tribology Program Review, Dayton, OH, June 1997.

2. "New Concepts in Nanofabrication", Cambridge Healthtech Institute's Nanotechnology: Materials, Manufacturing and Applications Conference, San Francisco, CA, June 1997.

3. "One-Dimensional Nanostructures: Rational Synthesis, Novel Properties and Higher Order Structures", Gordon Research Conference on Inorganic Chemistry, Newport, RI, July 1997.

4. "One-Dimensional Nanostructures: Synthetic Approaches and Physical Properties", Gordon Research Conference on Clusters, Nanocrystals & Nanostructures, Plymouth, NH, July 1997.

5. "Growth, Structure and Properties of Carbide Nanorods", Norton/Saint-Gobain Industrial Ceramics, Inc., Northboro, MA, August 1997.

6. "Chemical Force Microscopy", Microscopy & Microanalysis '97, Cleveland, OH, August 1997.

7. "One-Dimensional Nanostructures: Chemistry, Physics and Applications", University of Pennsylvania, Philadelphia, PA, October 1997.

8. "Chemical Force Microscopy: Imaging and Manipulating Biological Materials", After the Genome 3, Santa Fe, New Mexico, October 1997.

9. "Growth and Physical Properties of One Dimensional Nanostructures", Michigan State University, East Lansing, MI, December 1997.

10. "One-Dimensional Nanostructures: Chemistry, Physics and Applications", James Franck Institute, The University of Chicago, Chicago, IL, December 1997.

11. "Energetic Deposition of Amorphous Tetrahedral Carbon Nitride Films", Materials Research Society Fall Meeting, Boston, MA, December 1997.

12. "Chemical Force Microscopy: Probing Molecules and Macromolecules at the Nanometer Scale", US-Japan Cooperative Program on Photoconversion and Photosynthesis, Napa, CA, January 1998.

13. "Nanostructures and Nanostructured Materials", 1998 American Association for the Advancement of Science Annual Meeting, Philadelphia, PA, February 1998.

14. "Chemical Force Microscopy: Probing Molecules and Macromolecules at the Nanometer Scale", Hutchinson Memorial Lecture, University of Rochester, Rochester, NY, February 1998.

15. "Synthesis of Nanostructures and Nanostructured Materials", Hutchinson Memorial Lecture, University of Rochester, Rochester, NY, February 1998.

16. "A Merger of Chemistry and Physics: Probing the Novel Properties of Nanotubes and Nanowires", Hutchinson Memorial Lecture, University of Rochester, Rochester, NY, February 1998.

17. "Measuring Adhesion Forces Between Model Monolayers and Polymer Films by Chemical Force Microscopy", 21st Annual Meeting of the Adhesion Society, Savannah, GA, February 1998.

18. "Chemical Force Microscopy: Probing Molecules and Macromolecules at the Nanometer Scale", University of Connecticut, Storrs, CT, March 1998.

19. "Chemistry and Physics in 1D: Growth, Properties and Applications of Nanowires and Nanotubes", University of California at Los Angeles, Los Angeles, CA, April 1998.

20. "Chemical Force Microscopy: Probing Molecules, Macromolecules and Molecular Assemblies on the Nanometer Scale", University of Washington, Seattle, WA, April 1998.

21. "One-Dimensional Nanostructures: Novel Properties of Nanotubes and Nanowires", Department of Physics, University of California at Berkeley, Berkeley, CA, April 1998.

22. "Chemistry and Physics in 1D", Department of Chemistry, University of California at Berkeley, Berkeley, CA, April 1998.

23. "Chemistry and Physics in 1D: Synthesis, Properties and Applications of Nanostructures", Materials for the 21st Century and Beyond, 12th Annual Symposium of the Center for Study of Gene Structure and Function, Hunter College, New York, NY, April 1998.

24. "Rational Growth of Nanowires Using Laser-Generated Nanoclusters", Gordon Research Conference on Laser Interactions with Materials, Andover, NH, June 1998.

25. "Nanotribology, Nanomechanics and New Molecular Probes", Air Force Office of Sponsored Research/Office of Naval Research Tribology Program Review, Annapolis, MD, June 1998.

B. CONSULTATIVE AND ADVISORY FUNCTIONS.

1. Associate Member, International Union of Pure and Applied Chemistry (1998)
2. Member, Editorial Advisory Board, Advanced Materials (1998)
3. Member, Editorial Advisory Board, *Chemistry of Materials* (1997)
4. Member, Editorial Advisory Board, *Chemistry: A European Journal* (1994)

C. TRANSITIONS.

Carbon nitride films for tribology applications. Dr. Bal K. Gupta, Seagate Technology, 7801 Computer Avenue, Bloomington, Minnesota 55435; (612)884-7867. Desirable friction/wear characteristics in carbon nitride films identified in studies at Harvard have been proposed for coatings of hard-disk sliders. The P.I.'s group has coated ~40 sliders for testing at Seagate.

VII. NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES.

1. C.M. Lieber, Z. John Zhang and C. Niu, "Covalent Carbon Nitride Material Comprising C_2N and Formation Method," 08/477,194; all claims have been allowed; awaiting issue of patent.

VIII. HONORS/AWARDS.

1. Fellow of The American Association for the Advancement of Science (1997)